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(54) Title: ELASTOMERIC FILM GRADE THERMOPLASTIC POLYMER COMPOSITIONS HAVING IMPROVED ELASTIC PERFORMANCE

(57) Abstract: The present invention relates to an elastomeric film grade thermoplastic polymer composition having improved elastic performance which comprises (a) from 52 to 60 percent by weight of a block copolymer having at least two polystyrene end-blocks and a mid-block of a hydrogenated polymerized diene which has a vinyl content of 45 percent by weight or less, (b) from 13 to 22 percent by weight of polystyrene, and (c) from 19 to 28 percent by weight of oil wherein (a) + (b) + (c) add up to 100 percent by weight.

ELASTOMERIC FILM GRADE THERMOPLASTIC POLYMER COMPOSITIONS HAVING IMPROVED ELASTIC PERFORMANCE

Field of the Invention

The present invention relates to elastomeric film grade thermoplastic polymer compositions, more specifically to such compositions that are extruded as films for use in disposable hygiene products such as adult, infant, and feminine hygiene products.

Background of the Invention

Extrudable elastomeric compositions which can be easily made into elastic films having low stress relaxation, low hysteresis, and high recoverable energy are described in United States Patents Nos. 4,663,220, 4,789,699, 4,970,259, or 5,093,422. Those elastomeric films are useful in making a variety of applications such as diaper waistbands and non-woven fabrics.

Polystyrene-poly(ethylene-butylene)-polystyrene elastomeric block copolymers (SEBS) and polystyrene-poly(ethylene-propylene)-polystyrene (SEPS) elastomeric block copolymers have been blended with other materials to form extrudable elastomeric compositions which can be more easily extruded into elastic films having improved processing properties. For example, they have been blended with polyolefins, such as polypropylene and polyethylene, and oils. While the additives improve the extrusion properties of the compositions and the processing properties of the elastic films, such additives have an adverse affect on the elastic properties of the resulting film, especially at temperatures above 25 °C.

The currently used commercial SEBS-based compounds for elastomeric films generally have an average stress relaxation, when measured on a film in the direction that

is transverse to the machine direction and tested at 100 °F (37.8 °C) at 150 percent elongation, of greater than 27 percent, and a retained tension or load of less than 105 psi (7.2 bar). Measurement in the transverse direction is the most important because when the film is assembled into the final product, it is the direction that gets stressed. Since these films are mainly used in disposable hygiene products, they have to be able to retain their properties at body temperature when stressed. Stress relaxation refers to the percent loss of tension or load encountered after elongating an elastic material at a specified rate of extension to a predetermined length. It is expressed as a percentage loss of the initial load encountered at a specified extension of the elastic material. For this application, the lower the stress relaxation the better. Higher retained tension or load, i.e. above 125 psi (8.6 bar), will allow the use of thinner films.

Summary of the Invention

The present invention is an improved block copolymer composition for extruding films having excellent stress relaxation and increased retained tension or load at elevated temperatures. The composition is comprised of
(a) from 52 to 60 percent by weight of a block copolymer having at least two polystyrene end-blocks and a mid-block of a hydrogenated polymerized diene which has a vinyl content of 45 percent by weight or less,
(b) from 13 to 22 percent by weight of polystyrene, and
(c) from 19 to 28 percent by weight of oil,
wherein (a) + (b) + (c) add up to 100 percent by weight.

Detailed Description of the Invention

The extrudable elastomeric composition of the present invention is an improvement of the extrudable compositions described in United States Patents Nos. 4,970,259 and 5,093,422. The known compositions include one or more

styrenic block copolymers, typically a polystyrene-poly(ethylene-butylene)-polystyrene (S-EB-S) or a polystyrene-poly(ethylene-propylene)-polystyrene (S-EP-S) elastomeric block copolymer which is produced by hydrogenating a polystyrene-polybutadiene-polystyrene or polystyrene-polyisoprene-polystyrene block copolymer. The extrudable compositions further comprise a polyolefin and an extending oil.

The styrenic block copolymers have at least two polystyrene blocks, preferably separated by a hydrogenated block of polybutadiene (EB). Suitably, the block copolymer is a polystyrene-polybutadiene-polystyrene tri-block copolymer with a molecular weight between 60,000 and 120,000, preferably between 80,000 and 110,000 and a polystyrene content (PSC) of 10 to 30 percent by weight, preferably of 14 to 25 percent by weight, wherein at least 80 percent, preferably at least 90 percent of the butadiene double bonds are hydrogenated. The block copolymers of this invention preferably comprise polystyrene end-blocks each having a number average molecular weight of 7,000 to 11,000 and saturated polybutadiene mid-blocks having a number average molecular weight of 70,000 to 90,000. Most preferably, the block copolymer is a hydrogenated block copolymer, polystyrene-poly(ethylene-butylene)-polystyrene (SEBS), having a polystyrene content of 14 to 25 percent by weight, a polystyrene block number average molecular weight of 7000 to 11,000, a polybutadiene block number average molecular weight of 70,000 to 90,000, and a vinyl content of 45 percent by weight or less.

The term "vinyl content" refers to the content of a conjugated diene that is polymerized via 1,2-addition (in the case of butadiene - it would be 3,4-addition in the case of isoprene), instead of via 1,4-addition. The term

"vinyl" refers to the presence of a pendant vinyl group on the polymer chain.

These polymers may be prepared using free-radical, cationic and anionic initiators or polymerization catalysts. Such polymers may be prepared using bulk, solution or emulsion techniques. In any case, the polymer containing at least ethylenic unsaturation will, generally, be recovered as a solid such as a crumb, a powder, a pellet, or the like.

These tri-block copolymers may be made by sequential polymerization, but also by coupling di-block copolymers (which may, but need not be identical).

The styrenic block copolymers must be hydrogenated. In general, the hydrogenation or selective hydrogenation of the polymer may be accomplished using any of the several hydrogenation processes known in the prior art. For example the hydrogenation may be accomplished using methods such as those taught, for example, in US Patent Nos. 3,494,942; 3,634,594; 3,670,054; 3,700,633; and Re. 27,145. The methods known in the prior art and useful in the present invention for hydrogenating polymers containing ethylenic unsaturation and for hydrogenating or selectively hydrogenating polymers containing aromatic and ethylenic unsaturation, involve the use of a suitable catalyst, particularly a catalyst or catalyst precursor comprising an iron group metal atom, particularly nickel or cobalt, and a suitable reducing agent such as an aluminium alkyl.

In general, the hydrogenation will be accomplished in a suitable solvent at a temperature within the range from 20 to 100 °C and at a hydrogen partial pressure within the range from 100 to 5,000 psig (6.9 to 344.7 bar g), preferably 100 to 1,000 psig (6.9 to 68.9 bar g). Catalyst concentrations within the range from 10 to 500 ppm (wt) of iron group metal based on total solution are generally

used and contacting at hydrogenation conditions is generally continued for a period of time within the range from 60 to 240 minutes. After the hydrogenation is completed, the hydrogenation catalyst and catalyst residue will, generally, be separated from the polymer.

The compound of this invention contains from 52 to 60 percent by weight of the above block copolymer. It is important that the total amount of polymer in the compound be between 52 to 60 percent by weight of the compound. If this condition is not satisfied, then the compound will have stress relaxation values greater than 27 percent when the polymer content is below 52 percent and the compound will not be processable into thin films (0.001-0.020 inches or 0.025-0.508 mm thick) when the polymer content is above 60 percent.

The compound should contain from 13 to 22 percent by weight of polystyrene because it is compatible with the styrene end blocks of the polymer, which helps to increase the retained tension or load, and it also aids in the processing of the final compound. The polystyrene used in the compound of the present invention may be one which has a number average molecular weight of from 150,000 up to 400,000, most preferably 200,000 to 300,000, and a melt flow index from 1 to 18, preferably 1 to 7, ASTM D1239, condition G.

The amount of oil used in the compound ranges from 19 to 28 percent by weight because it aids in the processing of the final compound and helps reduce the amount of stress relaxation. If the oil content is not within this range, then the stress relaxation will be greater than 27 percent when the percentage of oil is less than 19 percent and the retained tension or load will be below 105 psi (7.2 bar) when greater than 29 percent. Oils which can be used are those which are compatible with the elastomeric mid-block segment of the elastomeric block copolymer and

which do not tend to go into the aromatic end-block portions to any significant degree. Thus, the oils can be viewed as paraffinic. Paraffinic oils which may be used in the elastomeric composition should be capable of being melt processed with other components of the elastomeric composition without degrading. Particularly important is the ability of the final composition to be melt extruded. An exemplary extending oil is a white mineral oil available under the trade designation DRAKEOL 34 from the Pennzoil Company Pennreco Division (DRAKEOL is a trademark). DRAKEOL 34 has a specific gravity of 0.864-0.878 at 60 °F (15.6 °C), a flash point of 460 °F (238 °C), and viscosity of 370-420 SUS at 100 °F (37.8 °C). Suitable vegetable oils and animal oils or their derivatives may also be used as the extending oil.

While the principal components of the extrudable elastomeric composition used to form the elastic sheet have been described in the foregoing, such extrudable elastomeric composition is not limited thereto, and can include other components not adversely affecting the extrudable elastomeric composition attaining the stated objectives. Exemplary materials which could be used as additional components would include, without limitation, pigments, antioxidants, stabilisers, surfactants, waxes, flow promoters, solvents, particulates, and materials added to enhance processability and pellet handling of the composition.

The term "elastic" is used herein to mean any material which, upon application of a biasing force, is stretchable, that is, elongatable to at least 400 percent of its relaxed unbiased length and which will recover to within 140 percent of its original unbiased relaxed length upon release of the stretching, elongating force.

As used herein, the term "stress relaxation" refers to the percent loss of tension or load between the maximum

load or force encountered after elongating an elastic material at a specified rate of extension to a predetermined length (or the load or force measured at some initial length) and the remaining load or force measured after the sample has been held at that length for a specified period of time, for example, from 0 to 60 minutes. Except where otherwise noted for the present invention, stress relaxation is expressed as a percentage loss of the initial load encountered at a specified extension of an elastic material. The stress relaxation is determined by calculating the difference between the initial maximum load measured after elongating an elastic material in the transverse direction at a rate of 20 inches (50.8 cm) per minute to an elongation of 150 percent (i.e., to 150 percent of the material's initial width) and the remaining load measured after that sample was held at that width for 60 minutes divided by the initial maximum load at that width. Testing may be performed on an Instron Model 5565 Universal Test Machine specimens based on ASTM D882. Stress relaxation after 60 minutes at, for example, an elongation of 150 percent (i.e., to 150 percent of the material's initial width) may be expressed as a percentage utilizing the following equation:

stress relaxation = (peak $load_{150\%}$ - $load_{150\%}$ @ 60 min)/(peak $load_{150\%}$)*100.

As used herein, the "number average molecular weight" was determined utilizing gel permeation chromatography techniques. All molecular weights are measured prior to hydrogenation which will increase the molecular weights by a small amount.

As used herein, the polystyrene content of a block copolymer refers to the %weight of polystyrene in the block copolymer. It is calculated by dividing the sum of

molecular weight of all polystyrene blocks by the total molecular weight of the block copolymer.

Example 1

Polymer A, a block copolymer, was made by standard solution anionic techniques followed by hydrogenation. The molecular weights of the blocks of this SEBS polymer were 9,200-72,300-9,400. Its vinyl content was 38 percent and its total styrene content was 20.2 percent.

Compound 1 was made by pre-blending 57.79 percent Polymer A with 17.26 percent Chevron EA3000 polystyrene having a melt flow of 1.8 grams/10 min. and a number average molecular weight of about 300,000 and 24.08 percent DRAKEOL 34. This pre-blend was then extruded on a Baker Perkins MPC/V-50 MKIII compounding line (which consists of a 32 mm co-rotating twin screw side feeder and a 75 mm crosshead extruder) at 425 °F (218 °C). The finished Compound 1 was then cast into 0.0025-0.0035 inch (0.0635-0.0889 mm) thick films on a Killion 30:1 KL100 1 inch (2.54 cm) extruder with a 10 inch (2.54 dm) film die. The die temperature was 420 °F-450 °F (216 °C-232 °C). The stress relaxation and retained tension or load of the cast film sample based on the Compound 1 was measured by the procedure described above. The results are shown in Table 3 below.

Example 2 and Comparative Examples 3 and 4

Example 2 and Comparative Examples 3 and 4 were prepared as described in Example 1 with the exception that a styrenic resin, HERCULES PICCOLASTIC D125 (HERCULES PICCOLASTIC is a trademark), was used in Comparative Example 3 instead of polystyrene EA300. Polymers A and B are SEBS block copolymers within the scope of the present invention. Polymers C and D are comparative examples of commercial SEBS block copolymers, which have been used to make films. The polymers and formulations used for Examples 1 and 2 and Comparative

Example 3 and 4 are shown in Tables 1 and 2. The molecular weight is expressed in terms of the molecular weights of the different blocks of the polymers.

Table 1

Polymer	MW (x1000)	Vinyl Content (% wt)	PSC (% wt)
A	9.2-72.3-9.4	38	20.2
B	10-76.4-10	38	21.6
C	10-47-10	38	31
D	7-34.5-7	38	30

Table 2

Compound Formulation, %	1	2	Comparative 3	Comparative 4
Polymer A	57.79			
Polymer B		57.90		
Polymer C			24.02	
Polymer D			36.04	58.3
DRAKEOL 34 Oil	24.08	23.45	27.03	29.2
1.8 MFI Polystyrene	17.26	17.78		11.7
Styrenic Resin			12.01	
Antioxidant	0.87	0.87	0.9	0.9

The results of the stress relaxation tests, at 100 °F (37.8 °C), are shown in Table 3 below. It can be seen that the retained tension or load of the compounds which fall within the scope of the present invention, Compound 1 and Compound 2, are above 125 psi (8.6 bar) and higher than the formulations which are outside the scope of the present invention, Comparative Compounds 3 and 4. It can also be seen that the stress relaxation of Compound 2 is considerably less than the other formulations.

Table 3

Sample	Initial Load @150% Elongation, psi (bar)	Retained Load @150% Elongation after 60 min., psi (bar)	Stress Relaxation @150% Elongation after 60 min. (transverse direction)
1	179.67 (12.4)	132.3 (9.1)	26.38%
2	196.36 (13.5)	152.7 (10.5)	22.22%
C3	144.71 (10.0)	104.9 (7.2)	27.5%
C4	150.71 (10.4)	116.0 (8.0)	23.04%

Example 7 and Comparative Examples 5, 6, 8 and 9

In this experiment, another series of test on other compound formulations varying percentages of polymer B were performed. The compounds shown in Table 4 were prepared by the procedure described in Example 1.

Table 4

Compound FORMULATION,%	C5	C6	7	C8	C9
Polymer B	48.65	51.85	54.55	60.44	63.29
Mineral Oil	25.71	24.93	24.90	20.13	15.25
1.8 MFI Polystyrene	24.92	22.44	19.73	18.51	20.00
Antioxidant	0.72	0.78	0.82	0.92	0.96

The compounds in Table 4 were cast into films and the stress relaxation and the retained tension or load were measured at 100 °F (37.8 °C) by the procedures described above. It can be seen in Table 5 that when the percentage of polymer B is greater than 60 percent (Comparative Compounds 8 and 9), the compound cannot be processed into a film, and when the percentage of polymer B is less than

52 percent (Comparative Compounds 5 and 6), the stress relaxation is greater than 27 percent. The retained tension or load on Compound 7 (within the scope of the invention) is significantly higher than 125 psi (8.6 bar) and the stress relaxation is considerably less than 27 percent.

Table 5

Sample	Initial Load @150% Elongation, psi (bar)	Retained Load @150% Elongation after 60 min., psi (bar)	Stress Relaxation @150% Elongation after 60 min. (transverse direction)
C5	240.55 (16.6)	162.9 (11.2)	32.27%
C6	241.27 (16.6)	167.7 (11.6)	30.48%
7	176.31 (12.2)	136.2 (9.4)	22.73%
C8	Unable to cast into film		
C9	Unable to cast into film		

Comparative Examples 10-13

In this experiment, a series of compounds were made using Polymer B. The percentage of Polymer B was constant and the percentages of polystyrene and oil were varied. The compounds in Table 6 were prepared by the procedure described above.

Table 6

FORMULATION, %	C10	C11	C12	C13
Polymer B	57.90	57.90	57.90	57.90
Mineral Oil	18.45	13.45	28.45	33.45
1.8 MFI Polystyrene	22.78	27.78	12.78	7.78
Antioxidant	0.87	0.87	0.87	0.87

The compounds in Table 6 were cast into films and the stress relaxation and the retained tension or load were measured at 100 °F (37.8 °C) by the procedures described above. It can be seen in Table 7 that when the percentage of oil is below 19 percent and the percentage of polystyrene is greater than 22 percent (C10), the stress relaxation is greater than 27 percent even though the retained tension or load was significantly greater than 125 psi (8.6 bar). When the percentage of oil is above 28 percent and the percentage of polystyrene is below 13 percent (C12 and C13), the stress relaxation is significantly below 27 percent and the retained load is the same as Comparative Examples 3 and 4 or less. It also shows that when the percentage of oil goes below 14 percent and the percentage of polystyrene is greater than 27 percent (C11), the compound cannot be processed into film.

Table 7

Sample	Initial Load @150% Elongation psi (bar)	Retained Load @150% Elongation after 60 min., psi (bar)	Stress Relaxation @150% Elongation after 60 min. (transverse direction)
C10	265.07 (18.4)	187.3 (12.9)	29.34%
C11	Unable to cast into film		
C12	135.7 (9.4)	107.3 (7.4)	20.91%
C13	95.41 (6.6)	79.6 (5.5)	16.55%

CLAIMS

1. An elastomeric film grade thermoplastic polymer composition having improved elastic performance which comprises
(a) from 52 to 60 percent by weight of a block copolymer having at least two polystyrene end-blocks and a mid-block of a hydrogenated polymerized diene which has a vinyl content of 45 percent by weight or less,
(b) from 13 to 22 percent by weight of polystyrene, and
(c) from 19 to 28 percent by weight of oil
wherein (a) + (b) + (c) add up to 100 percent by weight.

2. The composition of claim 1 where the block copolymer is a polystyrene-polybutadiene-polystyrene tri-block copolymer with a molecular weight between 60,000 and 120,000 and a polystyrene content 10 to 30 percent by weight where at least 80 percent of the butadiene double bonds are hydrogenated.

3. The composition of claim 1 where the block copolymer is a polystyrene-polybutadiene-polystyrene tri-block copolymer with a molecular weight between 80,000 and 110,000 and a polystyrene content of 14 to 25 percent by weight, a polystyrene block number average molecular weight of 7,000 to 11,000 for each end-block, a butadiene block number average molecular weight of 70,000 and 90,000, and a vinyl content of 45 percent by weight or less where at least 90 percent of the butadiene double bonds are hydrogenated.

4. The composition of claim 1 where the polystyrene (b) has a molecular weight average of 150,000 to 400,000, and a melt index less than 20 grams/10 minutes.

5. The composition of claim 1 where the oil (c) is a paraffinic/naphthenic oil with a flash point greater than

450 F (232 °C) and a specific gravity greater than 0.860.

INTERNATIONAL SEARCH REPORT

Inten nal Application No
PCT/EP 00/09032

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L53/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C09D C09J C08J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 068 138 A (MITCHELL NEIL F ET AL) 26 November 1991 (1991-11-26) * claims 1,5-9,11-14 ; column 5, line 3-8 ; table 1 (comparative example 2 and examples 1-4) ; column 3, line 51-58 ; column 5, line 64 - column 6, line 5 ; column 6, line 14-18 * column 7, line 40-55 ---	1-5
X	US 4 970 259 A (MITCHELL NEIL F ET AL) 13 November 1990 (1990-11-13) * claims 1,2,4,5,7,8,10,15 ; column 5, line 3-8 ; table 1 ; column 3, line 51-58 ; column 5, line 64 - column 6, line 5 ; column 6, line 14-18 * column 7, line 43-55 ---	1-5

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search	Date of mailing of the international search report
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Form PCT/ISA/210 (second sheet) (July 1992)

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 4 772 657 A (AKIYAMA YOSHIKUNI ET AL) 20 September 1988 (1988-09-20) * claims 1,4,5,8,9,11,12,16,19 ; table 5, 4 ; column 6, line 32-64 ; column 5, line 26-58 ; column 10, line 37-46 ; column 10, line 7-18 ; column 4, line 1-6 * column 7, line 59 -column 9, line 39	1-5
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inten nal Application No
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